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EVALUATION OF EFFECTS OF NO, CO2, AND SAMPLING FLOW RATE ON ARSENITE PROCEDURE FOR MEASUREMENT OF NO2 IN AMBIENT AIR

M. E. Beard, et al

National Environmental Research Center
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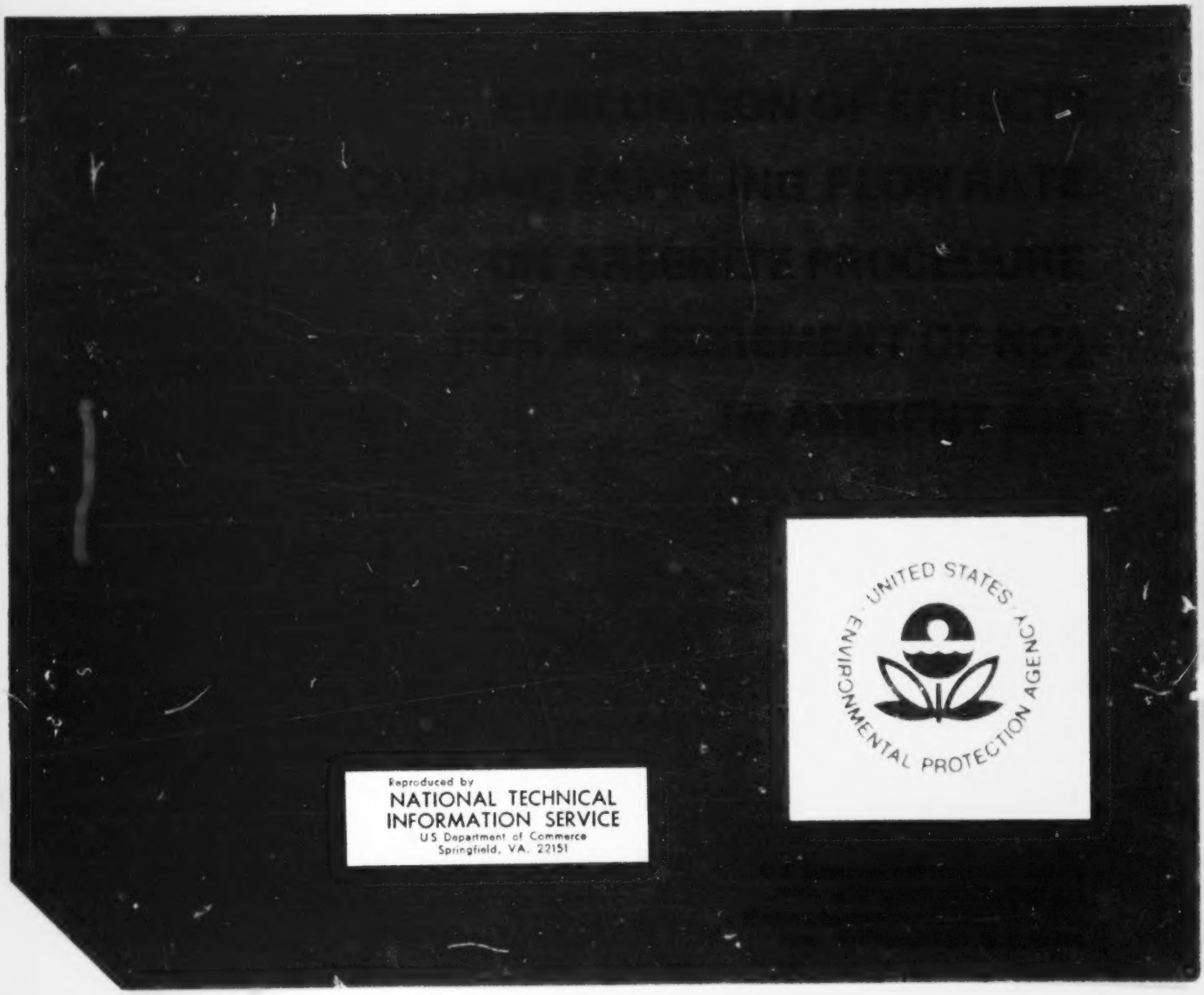

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16. ABSTRACT

The arsenite method for measurement of NO_2 in ambient air was investigated to quantify the effect of sampling flow rate and NO and CO_2 concentration on method response. NO and CO_2 were previously identified as positive and negative interferents in the method.

The results show that flow rates of 220 to 270 cm^3/min had no effect on the method response; higher flow rates decreased the method response. The flow rate range over which the method response is unaffected is considered adequate for ambient sampling.

Atmospheres containing NO_2, CO_2, and NO were sampled with the arsenite method in a 3x3x3 factorial experiment with five observations per cell. The concentrations were NO_2--50, 150, and 250 $\mu g/m^3$; NO--50, 180, and 310 $\mu g/m^3$; CO_2--200, 350, and 500 ppm. A statistical analysis of the resultant data shows that: (1) The method response is linearly related to changes in NO_2 level, as expected. Changes in levels of NO or CO_2 significantly change the slope of this linear relationship. (2) The method has an average positive bias of 9.9 $\mu g/m^3$ over all concentrations. The 95 percent confidence interval for this bias is +7.5 to 12.2 $\mu g/m^3$, and 3). The method response is related to the NO, CO_2, and NO_2 concentration by $y=4.36+1.12+0.0004\ (NO-CO_2)\ NO_2$. Over the concentration ranges cited above where: y = method response in $\mu g/m^3$, NO = NO concentration in $\mu g/m^3$, CO_2 = CO_2 concentration in ppm, and NO_2 = NO_2 concentration in $\mu g/m^3$.

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by

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ABSTRACT

The arsenite method for measurement of NO_2 in ambient air was investigated to quantify the effect of sampling flow rate and of NO and CO_2 concentration on method response. NO and CO_2 were previously identified as positive and negative interferents, respectively, in the method.

The results show that flow rates of 220 to 270 cm^3/min had no effect on the method response; higher flow rates decreased the method response. The flow rate range over which the method response is unaffected is considered adequate for ambient sampling.

Atmospheres containing NO_2, CO_2, and NO were sampled with the arsenite method in a 3x3x3 factorial experiment with five observations per cell. The concentrations were: NO_2 - 50, 150, and 250 $\mu g/m^3$; NO - 50, 180, and 310 $\mu g/m^3$; CO_2 - 200, 350, and 500 ppm. A statistical analysis of the resultant data shows that:

1. The method response is linearly related to changes in NO_2 level, as expected. Changes in levels of NO or CO_2 significantly change the slope of this linear relationship.

2. Over all concentrations, the method has an average positive bias of 9.9 $\mu g/m^3$. The 95 percent confidence interval for this bias is +7.5 to 12.2 $\mu g/m^3$.

3. The method response is related to the NO, CO_2, and NO_2 concentration by

$$y = 4.36 + [1.12 + 0.0004 (NO - CO_2)]NO_2$$

over the concentration ranges cited above where:

y = method response in $\mu g/m^3$

NO = NO concentration in $\mu g/m^3$

CO_2 = CO_2 concentration in ppm

NO_2 = NO_2 concentration in $\mu g/m^3$

The average bias introduced into the method by NO and CO_2 interference is small and does not necessitate applying a correction to data obtained with the method within the concentration range described.

CONCLUSIONS

A. Sampling Flow Rate

Nitrogen dioxide recoveries by the arsenite method using flow rates of 220 and 270 cm^3/min are the same; however, the recovery decreases 15 to 20 percent when the sample flow rate is increased from 270 to 380 cm^3/min. Flow rates above 270 cm^3/min should be avoided.

B. NO_2, NO, and CO_2 Experiment

The following conclusions are valid for the range of values specified in the experiment.

1. Method response is linear in relationship to changes in NO_2 levels, but changes in levels of NO or CO_2 significantly change the slope of the linear relationship.
2. Average method response changes significantly from level to level of CO_2 or NO, but the amount of change due to changes in CO_2 levels is not the same for each level of NO.
3. On the average, the method response is significantly higher than the actual NO_2 level by 9.89 $\mu g/m^3$.
4. The best linear equation of method response as a function of NO_2, NO, and CO_2 is

$$Y(\mu g/m^3) = 4.36 + [1.12 + .0004\ (NO\ \mu g/m^3 - CO_2\ ppm)]\ NO_2\ \mu g/m^3$$

C. Utility of the Method

The average bias introduced into the method by NO and CO_2 interference is small and does not necessitate applying a correction to data obtained with the method within the concentration range described.

EVALUATION OF EFFECTS OF NO, CO_2, AND SAMPLING FLOW RATE ON ARSENITE PROCEDURE FOR MEASUREMENT OF NO_2 IN AMBIENT AIR

I. INTRODUCTION

The arsenite procedure for the determination of nitrogen dioxide (NO_2) in ambient air has been evaluated earlier by EPA.[1] This evaluation showed the arsenite procedure to have a constant collection efficiency of 82.2 $\pm$4.5 percent. The evaluation also identified nitric oxide (NO) and carbon dioxide (CO_2) as positive and negative interferents, respectively. Sampling flow rate was also shown to affect the method response. In order to determine the utility of the arsenite method, the effect of these parameters needed to be defined. This work reports our efforts to quantify the effect of sampling flow rate and of NO and CO_2 concentrations on the arsenite method.

II. EXPERIMENTAL

A. General

The arsenite procedure used for this phase of the evaluation is described in Appendix A of the original report.[1] the method consists of drawing ambient air through a glass tube having a restricted orifice immersed in 50 ml of a solution containing 0.1 N NaOH and 0.1 percent w/w $NaAsO_2$. The NO_2 in ambient air is converted to nitrite ion. The concentration of nitrite is then determined colorimetrically by formation of a purple azo-dye.

The effect of sampling flow rate was measured by sampling test atmospheres at various sampling rates. The effect of NO and CO_2 concentrations was tested by sampling from test atmospheres containing various amounts of NO_2, NO, and CO_2. Each of the three test concentrations was held constant over the 24-hr sampling period. In each case, the response of the method to each variable was measured.

B. Test Atmosphere Generation

1. Nitrogen Dioxide

Test atmospheres containing known amounts of NO_2 were generated by diluting the effluent from gravimetrically calibrated NO_2-permeation devices with various measured volumes of purified air. This procedure has been described by O'Keeffe and Ortman,[2] and Scaringelli *et al.*[3,4] The permeation devices were made by the Microchemical Analysis Section of the National Bureau of Standards (NBS) and were calibrated frequently between sampling periods. The stability of permeation rates from these devices with respect to time has been well established.[5]

The temperature of the devices was controlled by a water-jacketed condenser which was maintained at 25.0 ±1° C by a Forma Temp Jr. constant temperature bath. This apparatus is shown in Figure 1. The NO_2 was flushed from the condenser by a flow of 100 cm^3/min dry N_2. The permeation devices had rates of 1.062 ±0.001 and 0.836 ±0.001 µg/min.

Purified air was obtained by passing compressed (House) air through silica gel for drying, treating with ozone to convert any NO to NO_2, and by passing through activated charcoal (6-14 mesh) and molecular sieve (6-16 mesh, type 4A) to remove NO_2 and hydrocarbons. Carbon dioxide was removed by passing the air through a trap containing approximately 1 kg of Ascarite (8-20 mesh asbestos particles impregnated with NaOH).

2. Nitric Oxide

Nitric oxide was added to the atmosphere by means of a "T" connection in the NO_2 system as shown in Figure 1. A Kjeldahl trap following the "T" insured mixing of the NO with the test atmosphere. A cylinder of NO in N_2 was analyzed by gas phase titration with O_3 as described in the Federal Register[6] and found to contain 92.4 ±3.1 ppm NO (113,700 µg/m^3). The NO concentration determined by the gas phase titration was verified by comparing, on a chemiluminescent NO-NO_2-NO_x monitor, the NO_2 produced during the titration with the output of an NO_2-permeation tube. The NO_2 concentrations from these two sources agreed within 2 percent. The cylinder was also

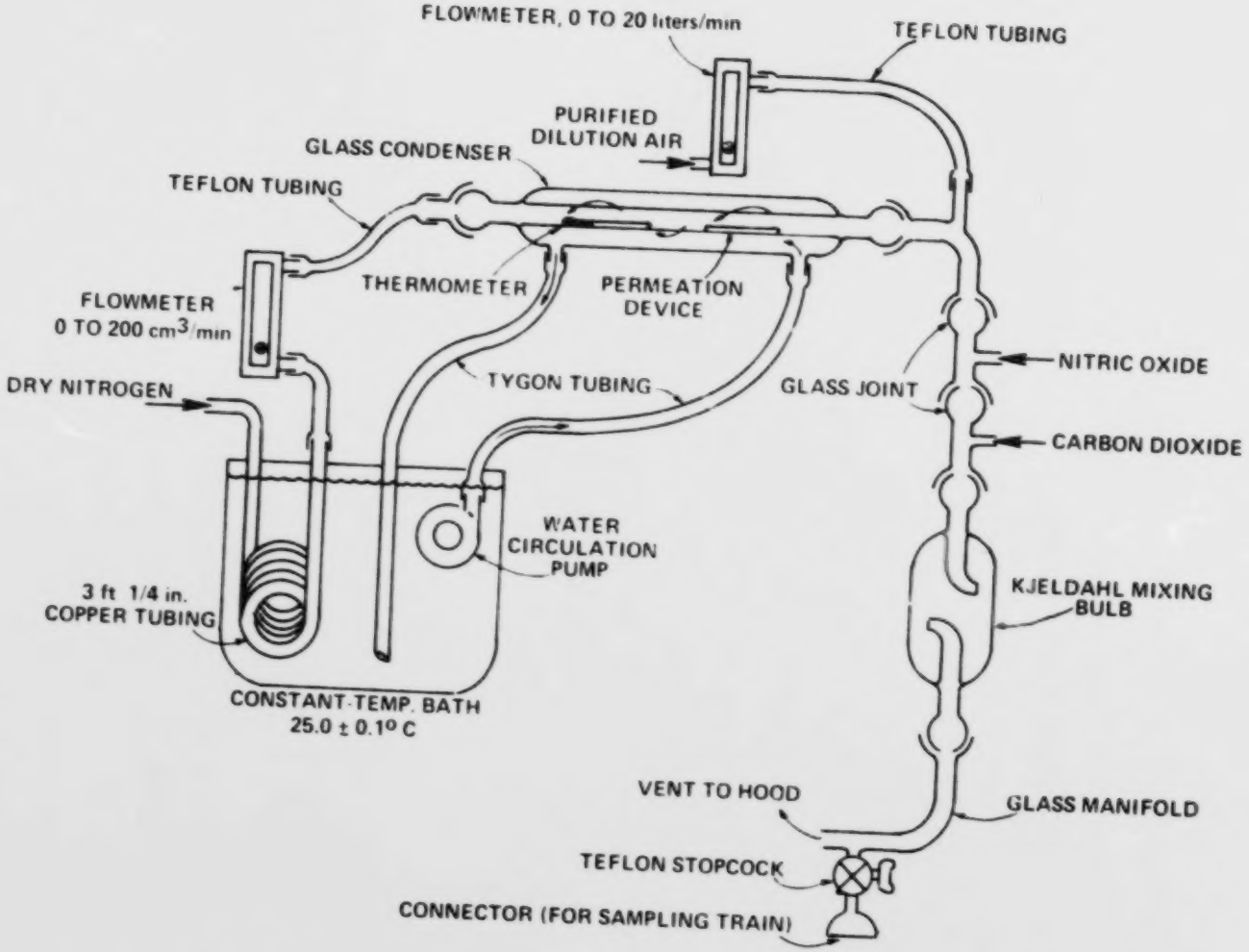

Figure 1. NO_2-NO-CO_2 atmospheric generation system.

analyzed for NO_2 impurity using the triethanolamine-guaiacol-sulfite (TGS) manual method[7,8] and found to contain 1.6 ±0.19 ppm NO_2 (2181 µg/m^3). Because of the NO_2 impurity in the NO cylinder it was necessary to calculate the exact NO_2 and NO concentrations using:

$$\frac{P.R.}{X} \times \frac{10^3 \ell}{m^3} + 2181 \frac{Y}{X} = \mu g\ NO_2/m^3 \qquad (1)$$

and

$$115{,}700 \frac{Y}{X} = \mu g\ NO/m^3 \qquad (2)$$

where:

P.R. = permeation rate of the NO_2 device (s), µg/min

X = total dilution air flow rate, ℓ/min

Y = NO flow rate, ℓ/min

The portion of the NO_2 coming from the NO cylinder was approximately 0.5 to 7.0 percent of the total NO_2 in the test atmosphere.

3. Carbon Dioxide

Carbon dioxide was added to the test atmosphere by means of a "T" connection, as in the addition of NO (See III.B. 2). The CO_2 was supplied from NBS Standard Reference Material 1674. These CO_2 cylinders contained 7.01 to 7.03 ±0.07 mole percent (70,100 to 70,300 ppm) CO_2. The CO_2 concentration of each cylinder was verified by Orsat analysis.[9] The cylinders were also checked for NO and NO_2 impurities by means of a chemiluminescent NO-NO_2-NO_x monitor. None was found. The CO_2 concentration in each

test atmosphere was calculated using:

$$\frac{F_{CO_2}}{F_{Total}} \times C_{CO_2} = C'_{CO_2} \qquad (3)$$

where:

F_{CO_2} = flow rate from CO_2 cylinder, ℓ/min

F_{Total} = combined flow rates in manifold, ℓ/min

C_{CO_2} = concentration of CO_2 added to test atmosphere, ppm

C'_{CO_2} = concentration of CO_2 in test atmosphere, ppm

As stated in III. B. 1., CO_2 was removed from the purified air by means of an Ascarite column. The purified air was tested for CO_2 by sampling the air with a bubbler containing a $Ba(OH)_2$ solution. No CO_2 was detected.

C. Sampling

Samples were collected in quintuplicate by attaching five sampling tubes to a common manifold. The flow rate for each tube was measured before and after sample collection as directed by the method. The total flow rate into the common manifold was also measured immediately before and after sampling and was compared with the sum of the individual flows to insure that there were no leaks in the system. Samples with a final flow more than 10 percent different from the initial flow were rejected.

D. Flow Control

1. $NO-CO_2$ Experiments

The samples collected for the $NO-CO_2$ experiments were collected at a rate of approximately 200 cm^3/min by using a 27-gauge hypodermic needle as a critical orifice as suggested by the method. A Gast Model 0211 oilless vacuum pump was used to maintain a pressure drop across the orifice of approximately 0.6-0.7 atmospheres. The total sampling time was about 20 hours.

2. Sampling Flow Rate Experiments

Flows of approximately 200 cm^3/min and 380 cm^3/min were obtained by using 27 and 26 gauge hypodermic needles, respectively, as critical orifices in the manner described above. A flow of approximately 270 cm^3/min was obtained by slightly crimping a 26 gauge needle until the desired flow rate was obtained. Again, the total sampling time was about 20 hours.

E. Analysis

After sampling was completed the tubes were disconnected from the manifold. Water lost by evaporation during the sampling was replaced, and an aliquot of the sample was analyzed as described in the method. A Beckman Model "B" Spectrophotometer was used for the absorbance measurements. A standard curve of μgNO_2^-/ml versus absorbance was determined for each experimental run.

III. RESULTS AND DISCUSSION

A. Sampling Flow Rate

In the previous evaluation,[1] the results of a ruggedness test show that increasing the flow rate from the value specified in the method write-up, 180-220 cm^3/min, to 300 cm^3/min produces a 14.4 percent decrease in the method response.

To quantify the effect of flow rate on method response, test atmospheres containing approximately 60 and 700 µg NO_2/m^3 were sampled at flow rates of approximately 220, 270, and 380 cm^3/min. The results are given in Table 1. The recoveries at flow rates of about 270 cm^3/min (106.7 and 107.2 percent) are essentially the same as the recoveries found at 220 cm^3/min (109.9 and 105.7 percent). At a flow rate of 380 cm^3/min the recovery was 89 percent which is a decrease of 19 percent. Thus, a decrease in recovery occurred between 270 and 380 cm^3/min.

Table 1. EFFECT OF SAMPLING FLOW RATE ON RECOVERY OF NO_2 IN THE ARSENITE PROCEDURE

NO_2 generated, µg/m^3	Sampling flow rate, cm^3/min	Percent recovery (NO_2 analyzed/NO_2 generated) x 100
51.9	381.7	89.3
60.3	388.6	89.7
666	382.6	89.2
63.3	267.6	106.7
671	267.6	107.2
63.5	224.6	109.9
663	224.5	105.7

Since a flow rate of 270 cm^3/min is considerably above the upper limit specified in the method, no tightening of the flow rate specifications is required.

It should be noted that the data in Table 1 show some NO_2 recoveries greater than 100 percent. This is due to removal of ambient CO_2 by the Ascarite scrubber such that the CO_2 concentration during these experiments was considerably less than the ambient CO_2 concentration present when the NO_2 collection efficiency (82 percent) was determined. The error in the method caused by determining the collection efficiency in the presence of ambient levels of CO_2 is somewhere between 0 and 3 percent. This statement is based on the results of a collaborative test of the arsenite method,[10] carried out in ambient air, which shows that the bias of the whole method is only -3 percent. Thus, the collaborative test indicates that any error in the collection efficiency as a result of the above "CO_2 effect" is quite small and does not justify redetermination of the collection efficiency.

A more detailed description of the effect of CO_2 on the method is given in the following sections.

B. NO and CO_2

1. Design

A series of experiments was conducted to quantify the effect of NO and CO_2 concentrations on the recovery of NO_2 by the arsenite method. Test atmospheres containing combinations of one of three levels, at a constant concentration of each substance, were sampled according to the method. Three levels were chosen to demonstrate the effect of each material and to show if the effects were

linear or curvilinear over the range of interest. This plan results in 27 experiments and a format for this study is shown in Figure 2.

Each NO, CO_2, and NO_2 concentration was held constant during an experiment, rather than varying the concentration with time as would be the case in ambient air, because it would have been difficult to accurately control the concentration under the latter conditions. It is believed that the constant-concentration

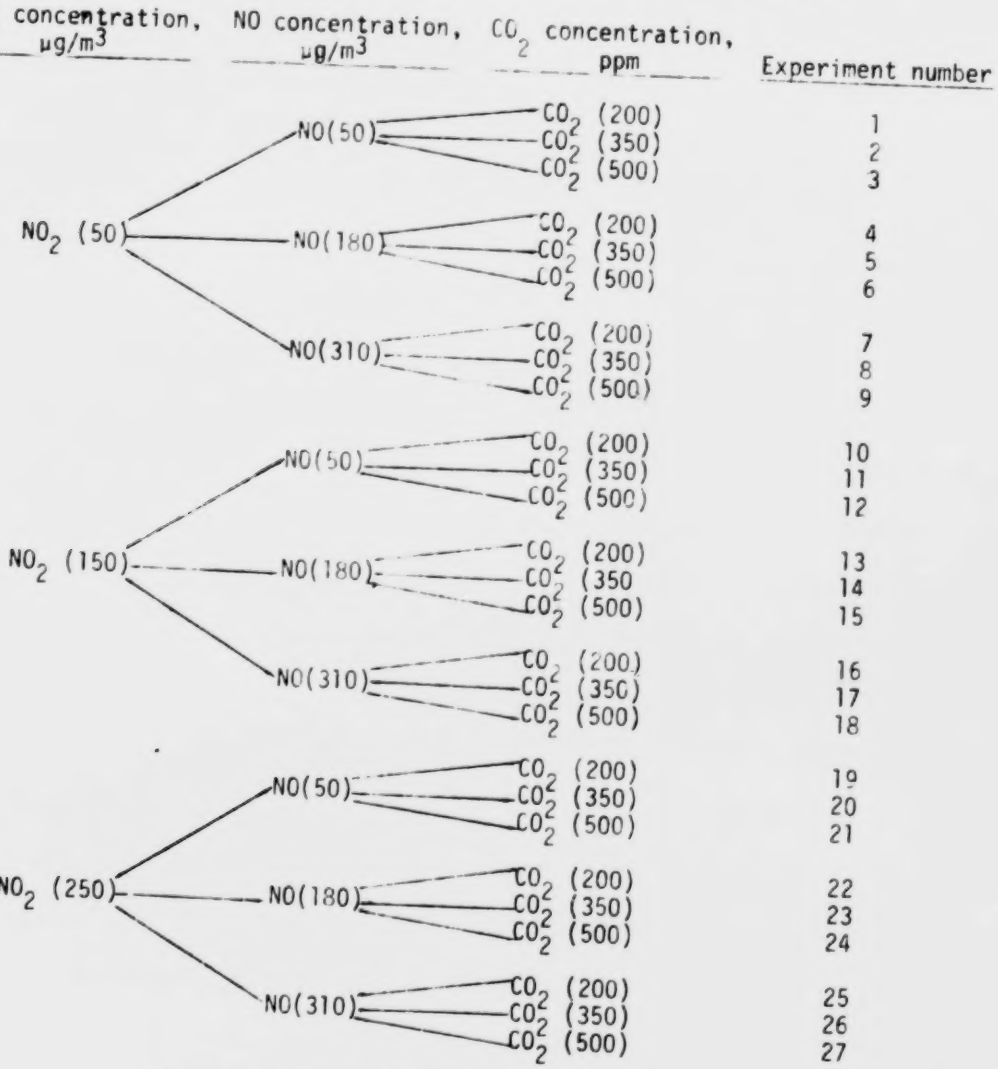

Figure 2. NO_2, NO, AND CO_2 STUDY FORMAT

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conditions represent a reasonable approximation to ambient conditions, and therefore, provide a useful means for evaluating interferences to the method.

Nitric oxide and NO_2 levels for the experiments were derived from examination of EPA NO_2 network data collected by chemiluminescence and continuous colorimetric procedures.[6] Carbon dioxide levels were derived from the literature[11] and from unpublished EPA data collected by a non-dispersive infrared (NDIR) method.[12]

Maximum, mid-range, and minimum concentrations were chosen for each of the three parameters and their nominal values are given in Table 2. The mid-range values were chosen to approximate average ambient NO and CO_2 concentrations and the ambient air standard for NO_2 (0.05 ppm).[13] Upper and lower levels were set approximately at the maximum and minimum 24-hour averages for the NO and NO_2 concentrations. The minimum CO_2 value is lower than ordinarily found in ambient air and was chosen to allow the ambient air average to be the mid-range value. Also, minimum values for NO and NO_2 were set at low concentrations rather than

Table 2. NO_2, NO AND CO_2 CONCENTRATIONS SELECTED FOR STUDY

	Minimum	Mid-range	Maximum
NO	50 $\mu g/m^3$ (0.04 ppm)	180 $\mu g/m^3$ (0.15 ppm)	310 $\mu g/m^3$ (0.25 ppm)
NO_2	50 $\mu g/m^3$ (0.03 ppm)	150 $\mu g/m^3$ (0.08 ppm)	250 $\mu g/m^3$ (0.13 ppm)
CO_2	200 ppm	350 ppm	500 ppm

their minimum ambient levels of 0 $\mu g/m^3$ since a concentration of zero would obviously have no effect on the method.

The experiments were conducted in random order with each atmosphere being sampled in quintuplicate. The data are given in Table 3. Column 1 of Table 3 lists the experiment number, and column 2 shows the random order in which the experiments were conducted. Columns 3 through 5 show the actual generated values of NO_2, NO, and CO_2. Columns 6 through 10 show the method response of the arsenite procedure to the generated values.

2. Analysis and Discussion of Results

a. Analysis of Variance

The data in Table 3 were generated according to a completely randomized 3x3x3 factorial design with five repeat samples per treatment combination. The sources of variation in the method response were identified in the analysis of variance, Table 4. Equal spacing of the generated NO_2 levels facilitated investigations about the linearity of the method response. For example, the two degrees of freedom for NO_2 in line one of Table 4 were divided into two single degree of freedom components for testing whether the method response is linear or quadratic in relation to changing NO_2 levels. The deviations of the acutal generated levels of NO_2, NO, and CO_2 from those given in Figure 2 are minimal. This is common for an experiment of this type and does not seriously affect the conclusions drawn from the analysis of variance. However, any linear relationships shown to be significant in the analysis of variance were determined by regressing the method response (Y) onto the actual generated NO_2 values rather than the nominal levels.

Table 3. RECOVERY OF NO_2 BY ARSENITE PROCEDURE AT GENERATED NO_2, NO, AND CO_2 LEVELS

Experiment number	Random order number	Generated NO_2, $\mu g/m^3$	Generated NO, $\mu g/m^3$	Generated CO_2, $\mu g/m^3$	Method response, $\mu g/m^3$ $NO_{2(1)}$	$NO_{2(2)}$	$NO_{2(3)}$	$NO_{2(4)}$	$NO_{2(5)}$
1	24	48.0	49.5	194.9	54.0	51.9	53.9	49.5	54.1
2	9	47.9	51.3	354.9	50.1	47.6	49.4	49.5	54.4
3	11	47.7	49.1	509.7	47.1	46.8	48.7	47.5	46.8
4	25	48.3	182.7	204.0	60.8	59.4	57.3	57.7	77.7
5	3	47.6	153.4	362.3	52.1	51.2	56.3	52.9	51.5
6	5	48.3	183.6	516.9	49.6	48.8	50.8	49.7	51.4
7	18	48.2	315.9	203.7	58.9	56.6	57.7	53.3	61.0
8	16	48.0	306.0	350.7	58.8	56.3	57.1	59.6	58.3
9	15	48.4	307.8	521.3	53.9	54.4	53.7	51.6	51.0
10	26	145.0	49.5	201.4	156.2	146.7	156.1	154.0	160.3
11	14	146.1	49.9	351.0	155.1	145.2	153.7	150.5	153.5
12	13	146.0	48.8	505.0	141.2	140.3	141.9	139.3	138.8
13	17	145.6	184.3	203.1	165.6	156.5	173.8	162.8	167.0
14	1	144.5	179.9	347.9	179.1	177.7	173.5	179.2	178.1
15	4	145.7	182.7	510.0	141.8	137.3	142.0	133.6	142.3
16	20	146.7	314.5	203.6	170.4	165.4	171.0	171.4	175.2
17	27	145.4	307.9	349.5	165.0	153.7	163.6	161.8	167.5
18	7	145.6	307.1	512.1	146.7	142.9	151.7	145.1	152.8
19	23	243.5	50.3	203.9	260.5	241.6	257.9	255.3	266.2
20	6	242.0	49.5	357.6	254.5	229.2	250.3	242.2	259.9
21	22	243.3	50.2	511.6	231.4	219.3	229.0	228.7	231.5
22	2	243.2	179.5	201.0	275.7	260.0	280.3	276.7	283.3
23	8	242.8	180.6	354.9	262.2	233.0	260.1	253.4	259.8
24	21	244.2	182.4	521.1	239.5	242.6	241.7	225.3	240.3
25	12	240.8	317.0	202.8	286.3	267.3	285.7	271.6	290.8
26	19	240.9	311.7	356.2	263.3	247.4	259.9	251.1	263.4
27	10	241.8	308.8	499.3	268.1	257.6	286.0	252.4	257.1

Table 4. ANALYSIS OF VARIANCE AND TEST FOR LINEARITY

Line	Source	D.F.	Sum of squares	Mean square	F
1	NO_2	2	915474.98	457737.49	10923.38
2	Linear	1	915365.02	915365.02	21846.42
3	Quadratic	1	109.95	109.95	2.62 N.S.
4	CO_2	2	7846.80	3923.40	93.62
5	NO	2	4369.60	2184.80	52.14
6	NO_2 x CO_2	4	2783.34	695.84	16.60
7	Linear x CO_2	2	2658.35	1329.18	31.72
8	Quadratic x CO_2	2	124.98	62.49	1.49 N.S.
9	NO_2 x NO	4	1382.19	345.55	8.25
10	Linear x NO	2	1216.78	608.39	14.50
11	Quadratic x NO	2	165.41	82.71	1.97 N.S.
12	CO_2 x NO	4	965.61	241.40	5.67
13	NO_2 x CO_2 x NO	8	1691.23	211.40	5.04
14	ERROR	108	4523.67	41.90	
	TOTAL	134	939039.41		

N.S. = not significant at the $\alpha = 0.05$ level.

From the second line in Table 4, the method response is significantly linear in fit over the range of generated NO_2 values and is given by

$$Y = 4.41 + 1.04\ (NO_2) \qquad (4)$$

From lines seven and ten in Table 4, this relationship is shown to remain linear but changes significantly in slope as the generated levels of CO_2 or NO change. The relationships between method response and generated NO_2 for each level of CO_2 are:

(200 ppm CO_2) $\quad Y = 4.48 + 1.09\ (NO_2)$

(350 ppm CO_2) $\quad Y = 7.45 + 1.03\ (NO_2)$

(500 ppm CO_2) $\quad Y = 1.20 + 0.99\ (NO_2)$

As the level of CO_2 increases, the slope decreases and the slopes are significantly different according to line seven of Table 4. The relationships between measured NO_2 and generated NO_2 for each level of NO are:

(50 $\mu g/m^3$ NO)	$Y = 3.24 + 0.99\ (NO_2)$
(180 $\mu g/m^3$ NO)	$Y = 7.24 + 1.03\ (NO_2)$
(310 $\mu g/m^3$ NO)	$Y = 2.54 + 1.09\ (NO_2)$

As the level of generated NO is increased the slope increases and the slopes are significantly different according to line ten of Table 4. The fact that the coefficients are the same in both sets of relationships but appear in reverse order for increasing NO levels as compared to increasing CO_2 levels is merely coincidental.

One must be careful not to extrapolate the method response to NO_2 values near the lower minimum detectable limit of 9 $\mu g/m^3$.[10] The values of the generated NO_2 levels are all some distance from this value and a straight line not going through zero proves to be the best fitting line. The explanation may be that the true relation between method response and generated NO_2 is curved near zero but this curvature is slight in the range within which the NO_2 is being generated.

The effect of different levels of NO and CO_2 on the method response at three different levels of NO_2 may be seen in Table 5. For instance, as the nominal CO_2 level is increased from 200 ppm to 350 ppm (75 percent increase), the average method response decreases by 7 percent, as seen in the lower margin. A further increase in the CO_2 level from 350 ppm to 500 ppm causes a further drop of 7 percent in

Table 5. AVERAGE VALUES OF METHOD RESPONSE[a]

NO, µg/m³ \ CO_2, ppm	200			350			500			
NO_2, µg/m³	50	180	310	50	180	310	50	180	310	
50	52.68	62.58	57.20	50.20	52.80	58.06	47.78	50.06	52.92	53.84
150	154.66	165.14	171.68	151.60	177.52	162.32	140.30	139.40	147.84	156.61
250	256.30	275.20	280.34	247.22	253.70	257.02	227.98	237.88	264.24	255.54
NO x CO_2	154.55	167.64	169.51	149.67	161.34	159.13	138.69	142.45	155.00	Grand mean
		163.90			156.72			145.38		155.26

*Each cell is the average of 5 values, and the right-hand and lower margins are the average of 45 method response values. The NO x CO_2 line represents the average of 15 values.

the average method response. However, for each level of NO, the decrease in average method response due to increasing CO_2 is not the same as seen in the NO x CO_2 margin. As the nominal NO level is increased from 50 $\mu g/m^3$ to 180 $\mu g/m^3$ (over 300 percent), the average method response increases by 6 percent. A further increase in the NO level from 180 $\mu g/m^3$ to 310 $\mu g/m^3$ (67 percent increase) results in a 3 percent increase in the average method response. These results are not readily seen in Table 5 without some additional averaging.

b. Bias the Precision

The overall bias of the arsenite method, calculated by taking the difference (method response - generated NO_2) and averaging over all 135 values, is +9.88 $\mu g/m^3$. The 95 percent confidence interval for this bias is (7.52 $\mu g/m^3$, 12.24 $\mu g/m^3$) indicating that this bias is real and significantly different from zero. However, the bias does not remain constant but is affected significantly by changes in NO and CO_2 as seen in the analysis of variance of this difference summarized in Table 6. As seen in Table 7, more than tripling the NO from 50 $\mu g/m^3$ to 180 $\mu g/m^3$

Table 6. ANALYSIS OF VARIANCE OF BIAS

Source	D.F.	Sum of squares	Mean square	F
NO	2	4553.68	2276.84	23.17[a]
CO_2	2	8053.30	4026.65	40.99[a]
NO x CO_2	4	977.41	244.35	2.49[a]
Error	126	12376.92	98.22	
Total	134	25961.32		

[a]Significant at the $\alpha = 0.05$ level.

Table 7. AVERAGE BIAS
($\mu g/m^3$)[a]

NO, $\mu g/m^3$	CO_2, ppm			
	200	350	500	
50	9.05	4.34	-6.98	2.14
180	21.94	15.79	-3.62	11.37
310	24.27	14.36	9.73	16.12
	18.42	11.5	-.29	9.88

[a]Each cell is the average of 15 values, and the margins represent the average of 45 values.

increases the overall bias five-fold from 2.14 $\mu g/m^3$ to 11.37 $\mu g/m^3$. A further increase of NO to 310 $\mu g/m^3$ increases the bias from 11.37 $\mu g/m^3$ to 16.12 $\mu g/m^3$ (approximately 42 percent). A significant decrease in bias is observed in going from level to level of increasing CO_2.

The smallest average positive bias is 4.34 $\mu g/m^3$ and this occurs when NO is at approximately 50 $\mu g/m^3$ and CO_2 is at 350 ppm. The smallest negative bias is -3.62 $\mu g/m^3$ and this occurs for NO at 180 $\mu g/m^3$ and CO_2 at 500 $\mu g/m^3$. Both of these values are not significantly different from zero at the $\alpha = 0.05$ significance level. This indicates that the method response is not significantly affected by these level combinations. The cell average of -6.98 $\mu g/m^3$ is also not significantly different from zero. All other cell averages in Table 7 are different from zero since their absolute value exceeds the upper 95 percent confidence limit of 7.09 $\mu g/m^3$ for averages of 15 values. The largest bias (+24.27 $\mu g/m^3$) occurs at low CO_2 levels (approximately

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